

Electron spin resonance investigation of Sc_2^+ in neon matrices and assignment of its ground electronic state as $X^4\Sigma^-$. Comparison with theoretical calculations

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The scandium radical cation, Sc_2^+ , has been isolated in neon matrices at 4 K and studied by electron spin resonance (ESR) spectroscopy and theoretical methods. It was produced by the x-irradiation of neon matrix samples containing neutral Sc_2 which was formed by trapping the products generated from the pulsed laser vaporization of scandium metal. The experimental and theoretical findings indicate that Sc_2^+ has a $^4\Sigma_g^-$ electronic ground state compared to an $X^5\Sigma_u^-$ state for the neutral scandium radical. The large decrease in the ^{45}Sc hyperfine interaction (A tensor) going from Sc_2 to Sc_2^+ provides direct experimental information concerning the types of valence molecular orbitals that are involved in these diatomic radicals. The neon matrix magnetic parameters for $^{45}\text{Sc}_2^+$ are $g_{\parallel} \approx 2.00$, $g_{\perp} = 1.960(1)$, $|A_{\parallel}| = 28(6)$, and $|A_{\perp}| = 26.1(3)$ MHz; the D value (zero field splitting) was 15 381(3) MHz. *Ab initio* configuration interaction (CI) calculations of the nuclear hyperfine interactions yielded results in reasonable agreement with the experimental observations.

I. INTRODUCTION

Neon matrix trapping at 4 K of scandium vapor generated from the pulsed laser vaporization of scandium metal produces an intense electron spin resonance (ESR) spectrum of the scandium radical, Sc_2 . Previous neon and argon ESR matrix studies have shown that Sc_2 has an $X^5\Sigma$ ground electronic state, derived essentially from a $4s\sigma^2 4s\sigma^1 3d\sigma^1 3d\pi^2$ configuration.¹ This experimental result is also consistent with several theoretical studies conducted on Sc_2 discussed below,²⁻⁶ which further identify the ground state as $X^5\Sigma_u^-$, deriving from a $4s\sigma_g^2 4s\sigma_u^1 3d\sigma_g^1 3d\pi_u^2$ configuration. The earlier experiments utilized a conventional high temperature effusion oven for scandium vaporization.¹ In the present experiments, x irradiation of neon matrices containing neutral Sc_2 produced by laser vaporization yields a new scandium radical species which is assigned to the $X^4\Sigma_g^-$ state of the high spin cation radical, Sc_2^+ , with a $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2$ configuration. The loss of 4s-type spin density in going from Sc_2 to Sc_2^+ is reflected in the large decrease in the magnitude of the $^{45}\text{Sc}(I=7/2)$ hyperfine interaction (A_{\perp} value) from 233 ± 3 to 26 ± 1 MHz. Theoretical calculations of the changes in the hyperfine interaction for Sc_2 and Sc_2^+ , conducted as part of this experimental study, are consistent with this observed large decrease in A for the cation radical.

The assignment of the observed ESR spectrum to the Sc_2^- radical anion was given serious consideration. Theoretical calculations conducted on the two lowest lying $^4\Sigma$ states of the anion indicated that one of these, the $^4\Sigma_g^-$ state with the configuration $4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^2 3d\pi_u^2$, did in fact, have a small scandium A_{iso} value and energy comparable to that calculated for the ground state of Sc_2^+ . However, given the electropositive nature of scandium and the observed photobleaching characteristics of the scandium radical being

observed, it was decided that the most reasonable ESR assignment is the scandium cation. Apparently no previous experimental or theoretical studies of Sc_2^- have been reported. Photoelectron spectroscopy on mass selected beams of the following diatomic transition metal anions have been conducted: Cr_2^- ,⁷ Fe_2^- ,^{8,9} Co_2^- ,⁸ Pd_2^- ,¹⁰ and Re_2^- .¹¹

In terms of electron count, Sc_2^+ is the simplest possible transition metal dimer cation. As such, it is especially important to determine its properties, so that other more complicated transition metal molecules can be understood. Other transition metal diatomic cation radicals studied experimentally by the matrix isolation ESR method include Mn_2^+ ,^{12,13} Co_2^+ and Ir_2^+ ,¹⁴ Nb_2^+ ,¹⁵ Cu_2^+ , Ag_2^+ and Au_2^+ .¹⁶ A great deal of electronic structure information has been obtained from previous matrix ESR studies of neutral transition metal diatomics and clusters.^{17,18} Recent examples include MoCu , MoAg , MoAu , WCu , WAg , WAu ,¹⁹ VNi , VPd , VPt , NbNi ,²⁰ ScNi , ScPd , YNi , YPd ,²¹ ScCr ,²² Co_3 , Rh_3 , Ir_3 ,¹⁴ and CrMn .¹³ Other small cation radicals recently studied in our laboratory include YAl^+ and YB^+ ,²³ CH_3OH^+ ,²⁴ C_2^+ ,²⁵ PdH_2^+ ,²⁶ Si_2^+ , and Ge_2^+ .²⁷

For most of the cation radicals studied the isolated counter anion is not a radical, and thus cannot be detected by ESR; an example would be OH^- . Recent results in our laboratory show that CO_2^- is also a fairly common background counter anion. We have conducted extensive ^{13}C and ^{17}O isotopic matrix experiments on this species (which can be detected by ESR) to determine optimum conditions for observing such isolated anion radicals.²⁸ We have employed a variety of generation methods for studying matrix isolated anion and cation radicals, including x irradiation of the matrix after deposition, laser surface ionization, electron bombardment, and irradiation of the matrix using an

open tube neon resonance lamp during the deposition process.^{24,28-31} Other anion radicals studied include F_2^- ,³² CH_2^- ,³³ and HI^- .²⁸ Electron transfer from sodium atoms has also been successfully employed for the generation of anion radicals in rare gas matrices.³⁴

In these scandium studies both the neutral dimer and the cation dimer have ground states that permit detection by ESR spectroscopy. This fortunate circumstance has not occurred in any of our previous ESR matrix ion studies for either the neutral-cation or the neutral-anion combination. An important experimental advantage of this situation is the ability to directly monitor the interconversion between the two radical types. Irradiation with x rays was shown to convert Sc_2 into Sc_2^+ .

Previous investigations in argon matrix experiments assigned certain absorption bands in the visible spectrum to electronic transitions of Sc_2 .³⁵ Resonance Raman spectroscopic measurements for Sc_2 in argon have determined a ground state vibrational frequency of $\omega_e'' = 239.9 \text{ cm}^{-1}$ and $\omega_{xe} = 0.93 \text{ cm}^{-1}$.^{35,36} An attempt to determine the bond strength of Sc_2 based on the Knudsen effusion mass spectrometric method yielded a third-law value of $D_0^0(\text{Sc}_2) = 1.12 \pm 0.22 \text{ eV}$,³⁷ however this method is well-known to be prone to error because of difficulties in estimating the electronic partition function for diatomic metals at temperatures near 2000 K.^{18,38,39} Application of the LeRoy-Bernstein method of analysis to the lowest six vibrational levels of Sc_2 isolated in argon, as observed by resonance Raman spectroscopy, provides $D_0^0(\text{Sc}_2) = 0.79 \text{ eV}$.³⁹ Although this value is inconclusive due to the limited number of vibrational levels observed, it is thought to provide a lower bound on the bond energy of Sc_2 .³⁹

In one of the first theoretical studies of Sc_2 , a local spin density calculation was performed on the series of homonuclear 3d series diatomics.² Although the predicted $^5\Sigma_u^-$ ground state was subsequently shown to be correct,¹ this investigation predicted the ground states of all of the 3d dimers to have extremely high spin multiplicities (predicting, for example, a $^{13}\Sigma_g^+$ ground state for Cr_2). Several subsequent calculations confirmed the identity of the ground state for Sc_2 as $^5\Sigma_u^-$,³⁻⁶ although this result was neither universally nor unambiguously obtained.⁴⁰⁻⁴² In the most detailed calculation to date, Åkeby, *et al.* have attempted to accurately determine the bond energy of Sc_2 through large scale internally contracted average coupled pair functional calculations which included the core 3p orbitals in the correlation treatment along with estimates of relativistic corrections.⁶ This undoubtedly represents the most thorough *ab initio* treatment available for the Sc_2 molecule, and presumably provides the most accurate description yet available. In the most accurate version of this calculation,⁶ the $^5\Sigma_u^-$ ground state of Sc_2 was found to have values of the vibrational frequency, ω_e , bond energy, D_e , and bond length, r_e , of 197 cm^{-1} , 0.77 eV , and 2.67 Å , respectively. Of these properties, only the vibrational frequency may be considered to be experimentally known, having the value $\omega_e = 239.9 \text{ cm}^{-1}$.³⁶ The discrepancy between this gargantuan calculation and the measured vibrational frequency illustrates the theoretical difficulties in de-

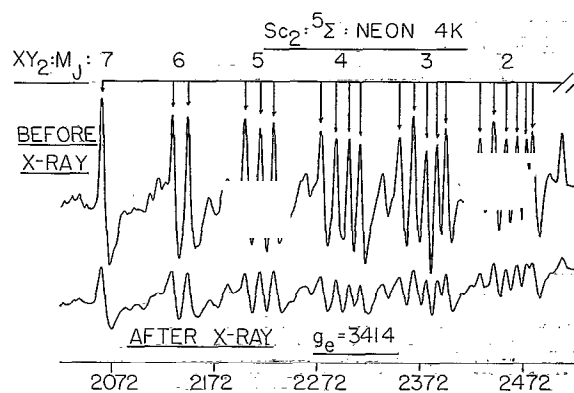


FIG. 1. The laser vaporization deposition of scandium metal in neon matrices produces the Sc_2 neutral radical. A small segment of the ESR spectrum of Sc_2 in its $^5\Sigma_u^-$ ground state is shown in the top trace before x irradiation. A detailed assignment of the ESR absorption features for Sc_2 in neon and argon matrices has been made in earlier work (Ref. 1). The lower trace shows the intensity decrease of the Sc_2 ESR signals caused by x irradiation at 80 keV for 50 min. The x-ray induced decrease in these Sc_2 ESR signals is accompanied by the appearance and growth of the Sc_2^+ ESR signals shown in Figs. 2 and 3.

scribing the properties of these types of molecules.

Previously studied small scandium radicals in rare gas matrices include ScO ,⁴³ Sc^{17}O ,²⁸ Sc_3 , Sc_{13} ,⁴⁴ ScH_2 ,⁴⁵ ScF_2 ,⁴⁶ and HScOH .²⁸ Experiments are currently under way in our laboratory to generate and characterize the high spin ScAl^+ and ScB^+ cations, to determine if they are similar to the previously studied YAl^+ and $\text{YB}^+(^4\Sigma^-)$ radicals.²³

II. EXPERIMENT

The ESR matrix isolation apparatus and the associated pulsed laser vaporization procedures used in our laboratory have been described previously.^{23,25-27} For these investigations, the copper matrix deposition surface was cooled to 4 K with a closed cycle helium refrigerator (APD 304 HS). Frequency doubled output from a Nd:YAG laser operating at 10 Hz and a typical energy of $\sim 20 \text{ mJ/pulse}$ was focused to a spot size of $\sim 0.5 \text{ mm}$ on the scandium metal surface (Alfa; 99.9% foil). The focusing lens was continuously moved during the matrix deposition process to prevent the drilling of deep holes in the scandium target which was located 5 cm from the matrix deposition surface. A typical deposit was conducted in this manner for 45 min with a neon flow rate of $5 \text{ std cm}^3 \text{ min}^{-1}$. See equipment diagram in Fig. 1 of Ref. 27.

Visible photolysis and x-irradiation of the matrix samples were conducted through a quartz window (5 cm diam and 3 mm thick) located 3 cm from the matrix sample. For the wavelength selective photolysis experiments, various Corning cutoff filters were mounted over this quartz access window. The x-irradiation equipment and procedure used in these scandium experiments have been described in a recent matrix ESR study of the methanol radical cation.²⁴ The beryllium window of the x-ray source was positioned $\sim 6 \text{ cm}$ from the quartz access window. The tungsten target in the x-ray tube was bombarded with 80 keV electrons

and x irradiation of the deposited matrix samples was typically conducted for 40 min. The matrix depositions and the subsequent photolysis and x irradiation were conducted with the deposition target out of the X-band ESR cavity. Following these various procedures the matrix sample was lowered into the microwave cavity for recording the ESR spectral changes produced.

III. RESULTS

A. ESR analysis

ESR spectra recorded for the neon matrices containing laser vaporized scandium showed all the absorption features previously observed for the neutral Sc_2 radical which has an $X^5\Sigma$ electronic ground state.¹ A segment of the Sc_2 ESR spectrum is shown in Fig. 1 for a neon matrix at 4 K. Similar laser vaporization experiments conducted with argon as the matrix did not produce the Sc_2 radical. The reduced diffusion rates of atoms in argon relative to neon is probably responsible for the lack of Sc_2 formation under these laser vaporization conditions. Higher scandium atom concentrations employed in the earlier argon experiments using a conventional high temperature effusion oven did produce Sc_2 in argon matrices.¹ The magnetic parameters for Sc_2 in neon and argon matrices are practically identical.

Each fine structure transition of Sc_2 is split into fifteen M_J hyperfine groups (two equivalent $I=7/2$ nuclei). Since the A_1 value for Sc_2 is large (233 MHz), the M_J groups are spread over a wide magnetic field range. The inner groups show higher order splittings since these M_J groups have different J origins where J is the quantum number representing the coupling of the two $I=7/2$ nuclei. For example, as shown in Fig. 1, the $M_J=5$ group of the XY_2 ($\Theta=90^\circ$) fine structure transition centered near 2215 G exhibits three equally intense lines since $M_J=5$ can originate from $J=7, 6$, and 5.

The substantial reduction in intensity of the Sc_2 ESR lines following x irradiation of the neon matrix sample is shown in the lower trace of Fig. 1. The Sc_2 spectra before and after x irradiation were recorded under the same instrumental conditions and no temperature change of the copper deposition surface occurred during the x-irradiation procedure.

As the neutral Sc_2 ESR signals grew weaker with x irradiation, a new 15 line hyperfine pattern shown in Fig. 2 centered near 1772 G appeared and became more intense as x irradiation continued, provided not all of the Sc_2 radicals had been consumed. These signals, which are assigned to the isolated Sc_2^+ radical in a 4Σ electronic ground state, were not present prior to x irradiation. The relative intensity distribution of this new 15 line pattern which has a small A_1 value of 10 G is that expected for two equivalent $I=7/2$ nuclei, namely 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1. In this case, the higher order splittings of the inner M_J components were not resolved since the A value is small. Other x-ray induced changes included the appearance of H_2O^+ and weak N_2^+ ESR signals in the g_e magnetic field region. The neon matrix ESR spectra of these commonly occurring background radical cations, which are nearly always

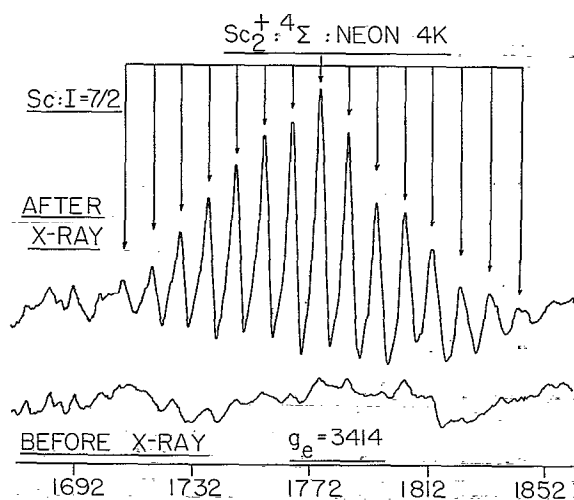


FIG. 2. The 15 line nuclear hyperfine pattern of the ESR spectrum assigned to the Sc_2^+ radical in a 4Σ electronic ground state is shown for a neon matrix sample at 4 K. The hyperfine lines result from two equivalent nuclei with $I=7/2$ for ^{45}Sc which has 100% natural abundance. This absorption feature is assigned to the XY_1 (perpendicular) fine structure transition, which may be compared to the overall simulated ESR spectrum of Fig. 4. The lower trace was recorded after the neon matrix deposition of laser vaporized scandium metal but prior to x irradiation of the deposited sample. The top trace was recorded after x irradiation at 80 keV for 50 min. As shown in Fig. 1, the Sc_2 neutral radical was present prior to x irradiation.

produced under ionizing conditions, have been previously assigned.²⁹⁻³¹ Isolated nonradical counter anions are probably produced by the x-irradiation treatment but not detected by ESR as discussed previously.

Extensive ESR scans under high gain/high sensitivity conditions between 0 and 9000 G also revealed a weak phase down absorption feature near 7760 G. This high field line shown in Fig. 3 appeared under the same experimental conditions required for the generation of the low-field 15 line pattern assigned to Sc_2^+ . Its microwave power response and photolysis effects described below also provided additional evidence that this high field line is part of the Sc_2^+ ESR spectrum. We assign this high field line to an off-angle (OA) absorption feature of Sc_2^+ as illustrated in the simulated ESR spectrum and accompanying H_{RES} vs Θ plots in Fig. 4. Efforts to detect the weaker XY_2 transition that lies at a higher magnetic field than the OA line were unsuccessful. The XY_N designation refers to the various perpendicular ($\Theta=90^\circ$) fine structure transitions that can be observed for a given high spin radical with the N subscript ordering these from low to high magnetic fields.²⁵

An analysis of these observed ESR features which are assigned to Sc_2^+ in a ground 4Σ state was conducted by an exact diagonalization of the following spin Hamiltonian:

$$\hat{H} = \beta_e \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - S(S+1)/3] + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S},$$

where all symbols have their standard meanings.²⁵ Our computer programs, which provide exact line fitting solutions to this Hamiltonian and produce simulated ESR spectra and H_{RES} vs Θ plots, have been previously described.^{25,30,31} By systematically varying g_1 and D (the

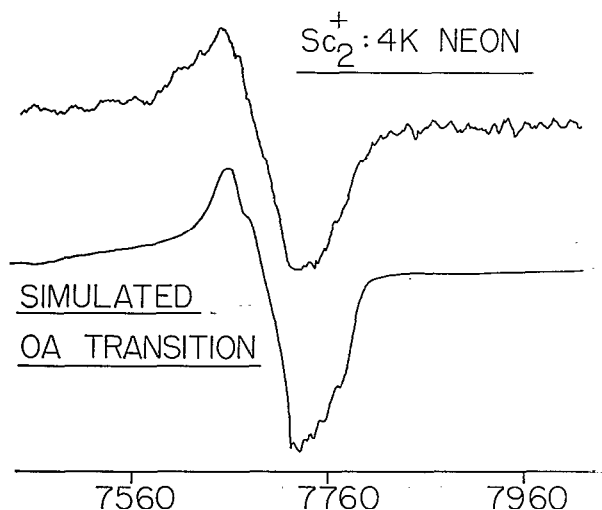


FIG. 3. An expanded scale presentation of the OA (off-angle $\Theta=25^\circ$) absorption feature of Sc_2^+ in a neon matrix sample at 4 K is shown in the top ESR spectrum. See overall spectrum in Fig. 4. A computer simulation of this OA feature is shown in the bottom ESR spectrum. Note that the linewidth, phase, and line shape of the simulated absorption exhibit close agreement with the observed spectrum.

zero field parameter), it was found that the OA absorption is observed at $\Theta=25^\circ$, which corresponds to the inversion in the H_{RES} vs Θ curve. The only assumption in this fitting process is that g_{\parallel} is close to g_e , which is a reasonable approximation.¹ The scandium A_{\perp} value can be obtained directly from the resolved 15 line nuclear hyperfine pattern on the low field XY_1 perpendicular absorption (see Fig. 2). Since the scandium hyperfine splitting on the OA line at $\Theta=25^\circ$ is determined by both A_{\perp} and A_{\parallel} , it was possible to estimate A_{\parallel} by carefully comparing simulated linewidths and line shapes with the observed line. The good

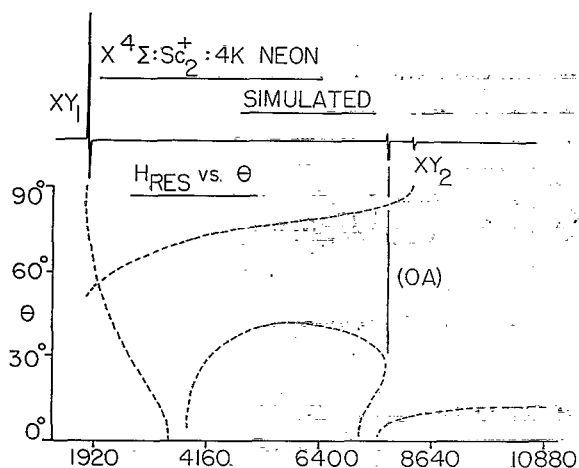


FIG. 4. The overall simulated ESR spectrum of Sc_2^+ in its $4\Sigma^-$ ground state is shown directly above its H_{RES} vs Θ plot, where Θ is the angle between the molecular axis and the applied magnetic field. These simulations do not include the small ^{45}Sc nuclear hyperfine interaction. Expanded scale presentations of the XY_1 perpendicular ($\Theta=90^\circ$) fine structure transition and the OA absorption feature at $\Theta=25^\circ$ are shown in Figs. 2 and 3, respectively.

quality of the agreement is shown in the expanded field presentation in Fig. 3. Unfortunately, the ^{45}Sc hyperfine structure on this OA line could not be resolved. However, if the best A_{\parallel} parameter for duplicating the experimental linewidth and line shape was varied by more than ± 5 MHz, the quality of the agreement was significantly reduced. The greater line width of this OA absorption probably results from the sensitivity of the inversion point to the D value, which is subject to matrix inhomogeneity. The XY_1 absorption is not sensitive to D once D becomes comparable in magnitude to the spectrometer frequency.

For a microwave frequency of 9567.5 ± 0.5 MHz, the calculated line positions of $XY_1=1776$ G and $OA=7722$ G agree within the experimental uncertainty of ± 0.5 G to the observed lines using $g_{\perp}=1.960(1)$, $g_{\parallel}=2.000$, and $D=15\,381(3)$ MHz. While the absolute signs of the ^{45}Sc A values cannot be determined from these experimental results alone, their magnitudes are $A_{\perp}=26.1(3)$ MHz and $A_{\parallel}=28(6)$ MHz. Assuming both A values are positive, we obtain $A_{\text{iso}}=27 \pm 2$ MHz and $A_{\text{dip}}=1 \pm 2$ MHz. If A_{\perp} were negative and A_{\parallel} positive, the A_{iso} and A_{dip} results would be -8 and 18 MHz, respectively. As discussed in the theoretical section, the calculated values of A_{iso} and A_{dip} , which must be considered highly approximate, fall within these experimental extremes. However, the important qualitative result is that A_{iso} is indeed quite small relative to A_{iso} for the neutral Sc_2 radical. The obvious theoretical reason for this decrease is the loss of scandium $4s$ character in the $4s\sigma_u^1$ molecular orbital which was present in neutral Sc_2 but which is lost upon ionization when Sc_2^+ is formed. The previously reported magnetic parameters for neutral Sc_2 are $g_{\parallel} \approx g_{\perp} \approx 2.00$, $A_{\parallel}=291(28)$, $A_{\perp}=233(3)$, and $D=3336(6)$ MHz.

B. Photolysis

Visible photolysis of the neon matrix samples reduced the ESR signals of Sc_2^+ and Sc_2 by at least 95% over a 30 min period. Such visible photolysis also sharply reduced the ESR lines of the isolated cation background radicals, namely, H_2O^+ and N_2^+ . Based upon previous studies of numerous matrix isolated radicals, it is unusual for neutral radicals to be photodestroyed by visible light. The photobleaching of charged radicals is a well established criteria for isolated ions. The photolytic energy typically exceeds the ionization energy of most of the isolated counter anions. The liberated electrons can easily diffuse throughout the rare gas lattice and neutralize the various cation radicals. For chemically bound or adjacent ion pairs (as opposed to isolated ions), photolysis in the visible region does not usually result in photodestruction.

In a separate series of matrix experiments, Corning cutoff filters were employed to determine the approximate wavelengths required to photodestroy these two scandium radicals. The ESR signal responses for Sc_2 and Sc_2^+ as a function of the various filters employed are presented in Fig. 5. The number of Sc_2 radicals present, as monitored by the XY_2 , $M_J=5$ ESR signals, is seen to decrease dramatically even when a CS-2-64 filter was used. This filter has a 50% transmittance (T) at ~ 665 nm and 1% T below 650

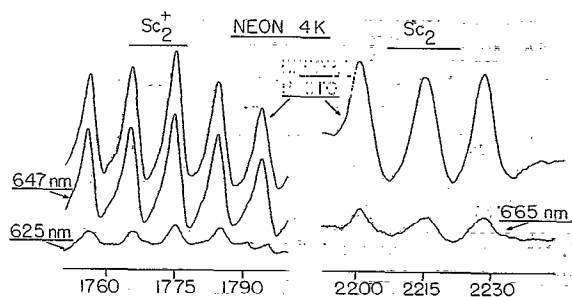


FIG. 5. The top ESR spectra were recorded for Sc_2^+ and Sc_2 in neon matrices at 4 K prior to visible light photolysis. The neutral Sc_2 ESR signals were substantially reduced in intensity by irradiation near 665 nm while higher energy irradiation near 625 nm was required to cause a similar reduction in the Sc_2^+ signals. The cutoff filter employed for 665 nm was a Corning CS-2-64, for 647 nm a CS-2-58 and for 625 nm a CS-2-60. The wavelength corresponding to approximately the 50% transmission level is cited.

nm. The Sc_2^+ ESR signals (XY_1 ; $M_J=2,1,0,-1,-2$) showed practically no decrease with a 2-64 or a CS-2-58 filter which has a 50% T at 647 nm and <1% T below 630 nm. However, the Sc_2^+ radicals are effectively eliminated when a CS-2-60 filter was employed; this filter has a 50% T at 625 nm and <1% T below 510 nm. For neutralization of the cations, a certain wavelength threshold is required for photoionizing the isolated counter anion. It is also possible that the direct photochemical destruction of the Sc_2^+ radical is occurring under these conditions. However, evidence against the direct photodestruction of Sc_2^+ were the observations that wavelengths in the 625–647 nm range caused moderate decreases in Sc_2^+ and small increases in Sc_2 , provided the time of exposure was kept to just a few minutes. This indicates that Sc_2^+ is being neutralized at a faster rate than Sc_2 is being photodestroyed. Based upon previous ESR anion studies in our laboratory,

irradiation at 647 nm would have photobleached a species such as Sc_2^- since it would be expected to have a small ionization energy. The absence of photodestruction at this wavelength strongly supports the cation assignment.

C. Calculations

Ab initio calculations were performed on the neutral scandium dimer Sc_2 , the cation Sc_2^+ , and the anion Sc_2^- in order to evaluate the relative energies of the electronic states of each species and to predict their hyperfine coupling constants. Considering the complexity of this problem we were constrained to use a rather small basis set in what must be considered only a preliminary theoretical analysis of these scandium radicals. The basis set⁴⁷ chosen was a double zeta contraction (8s5p3d) of Wachters (14s9p5d) set⁴⁸ augmented by an additional p function with an exponent of 0.0548 giving a final basis of (8s6p3d). This exponent was chosen so as to minimize the energy of the 4F excited state of the atom.

Geometry optimization for each electronic state was performed with the MELDF (Ref. 49) suite of programs at the self-consistent field (SCF) level in a point by point fashion. Relative energies of the electronic states and their hyperfine coupling constants were evaluated with single point Hartree–Fock single and double configuration interaction (HFSDCI) calculations at the optimized geometries. In the configuration interaction (CI) calculations all single excitations from the reference configurations were kept but only those double excitations which exceeded a threshold energy, evaluated by a perturbation theory approach, of 1×10^{-6} a.u. were retained. The results of these calculations are presented in Table I.

Our calculations show that the ground state of Sc_2 is $^5\Sigma_u^-$ with an electron configuration of $4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^1 3d\pi_u^2$ in agreement with the earlier work of others.^{2–6} The unpaired electron in the $4s\sigma_u^1$ orbital, which is mainly com-

TABLE I. Calculated energies and properties of the Sc_2 , Sc_2^+ , and Sc_2^- radicals.^a

State	Configuration	r_e (Å)	Energy (a.u.)		⁴⁵ Sc hyperfine coupling (MHz)		
			SCF	HFSDCI (ΣC_i^2)	Est. full CI ^b	A_{iso}	A_{dip}
Sc_2							
$^5\Sigma_u^-$	$4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^1 3d\pi_u^2$	2.68	–1519.3434	–1519.0185 (0.89)	–1520.1105	211	7.1
Sc_2^+							
$^4\Sigma_g^+$	$4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2$	2.48	–1519.1635	–1519.8335 (0.89)	–1519.9334	–32	7.0
$^4\Sigma_u^-$	$4s\sigma_g^2 4s\sigma_u^1 3d\pi_u^2$	2.81	–1519.1659	–1519.8299 (0.89)	–1519.9262	378	5.2
$^4\Pi_g$	$4s\sigma_g^2 3d\sigma_g^1 3d\sigma_u^1 3d\pi_u^1$	3.08	–1519.2239	–1519.8450 (0.91)	–1519.9194
Sc_2^-							
$^4\Sigma_g^-$	$4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^2 3d\pi_u^2$	2.83	–1519.3613	–1520.0380 (0.89)	–1520.1439	21	8.5
$^4\Sigma_u^-$	$4s\sigma_g^2 3d\sigma_g^1 4s\sigma_u^2 3d\pi_u^2$	2.71	–1519.3020	–1519.9883 (0.88)	–1520.0950	236	–6.3

^aAll calculations were conducted with the MELDF suite of programs (Ref. 49).

^bA description of the “estimated full CI” calculation approach is given in Ref. 50.

posed of atomic $4s$ atomic orbitals, results in a large calculated value of A_{iso} of 211 MHz, in reasonable agreement with the experimental value of 252(11) MHz.¹ This is apparently the first comparison of a calculated A_{iso} value with the earlier experimental measurements for Sc_2 .

As the ESR results have unequivocally shown that the discandium radical being observed has a quartet electronic state, only the low lying $^4\Sigma$ and $^4\Pi$ states were investigated in detail for Sc_2^+ and Sc_2^- . It was found that the lowest lying $^2\Sigma$ and $^2\Pi$ states were less stable than these quartet states, although it is difficult to make such a comparison for the two different spin manifolds given the problem of properly treating the correlation energies for states of different spin multiplicity. As shown in Table I, at the SCF and HFSDCI levels the calculations show the $^4\Pi_g$ state to be more stable than either of the two $^4\Sigma^-$ states of Sc_2^+ . The energy gap between the lowest $^4\Sigma^-$ state and the $^4\Pi_g$ state becomes significantly smaller with the inclusion of CI, and the estimated full CI energy of the $^4\Sigma_g^-$ state is slightly lower than that of the $^4\Pi_g$ state. A description of the "estimated full CI" calculation method has been described in previous theoretical studies.⁵⁰ Hence we assign the ground state of Sc_2^+ to the $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2$ electron configuration giving a $^4\Sigma_g^-$ ground state. The calculated value of the Sc hyperfine of -32 MHz for this state is in reasonable accord with our experimental value of 26 MHz (the sign of the hyperfine coupling cannot be determined from these ESR results alone). The other $^4\Sigma_u^-$ state is predicted to be slightly less stable (by 1600 cm^{-1} using the estimated full CI energies) and to have a large value of $A_{\text{iso}}=378$ MHz, which is not consistent with the ESR measurements. The $^4\Pi_g$ state would not be observed by matrix isolation ESR due to large g tensor anisotropy, thus eliminating this state as the ground state of Sc_2^+ .

Since it is possible that Sc_2^- could form under our experimental conditions, calculations were also performed on the anion radical. These HFSDCI calculations summarized in Table I, give the ground state of Sc_2^- to be a $^4\Sigma_g^-$ with a $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2 4s\sigma_u^2$ electron configuration. This state shows a small A_{iso} value of 21 MHz, which is also consistent with our ESR experimental results. The other $^4\Sigma_u^-$ state arising from a $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2 4s\sigma_u^1$ electron configuration is less stable by 0.05 a.u. (11 000 cm^{-1}) and has a large scandium A_{iso} value of 236 MHz. Hence, it is not possible from these theoretical calculations alone to determine whether the discandium molecule being observed is the cation or anion radical. However, given the electro-positive nature of scandium and the higher photolytic energies required for photobleaching, it is much more likely that the Sc_2^+ ion is being observed rather than the Sc_2^- .

IV. DISCUSSION

In the present study the ground state of Sc_2^+ has been shown to be $^4\Sigma_g^-$, deriving from the $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2$ configuration. Similar ground electronic configurations have been found for many of the other early $3d$ series transition metal molecules that have been investigated, in the sense that they possess two $4s\sigma_g$ and no $4s\sigma_u^*$ electrons. Thus Ti_2

has been shown to have a $^3\Delta_g$ ground state deriving from a $4s\sigma_g^2 3d\pi_u^4 3d\sigma_g^1 3d\delta_g^1$ configuration.⁵¹ TiV has a $^4\Sigma^-$ ground state deriving from a $4s\sigma^2 3d\pi^4 3d\sigma^1 3d\delta^2$ configuration.⁵² V_2 has a $^3\Sigma_g^-$ ground state deriving from a $4s\sigma_g^2 3d\pi_u^4 3d\sigma_g^2 3d\delta_g^2$ configuration,^{53,54} and Cr_2 has a $^1\Sigma_g^+$ ground state which at least nominally derives from a $4s\sigma_g^2 3d\pi_u^4 3d\sigma_g^2 3d\delta_g^4$ configuration.⁵⁵⁻⁵⁷

In contrast to these molecules, Sc_2 and ScCr are somewhat unusual, having significant contributions from $4s\sigma^2 4s\sigma^*$ configurations. In the case of Sc_2 , the large hyperfine splitting associated with the ground $^5\Sigma_u^-$ state identifies it as primarily $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^4 4s\sigma_u^1$ in character,¹ while an ESR investigation of ScCr (which possesses a $^6\Sigma^+$ ground state) has shown it to consist of a mixture of the $4s\sigma^2 3d\sigma^2 3d\pi^2 3d\delta^2 3d\sigma^*$ and $4s\sigma^2 3d\sigma^2 3d\pi^2 3d\delta^2 4s\sigma^*$ configurations.⁵⁸ Without a doubt, the importance of $4s\sigma^2 4s\sigma^*$ configurations in scandium-containing neutral molecules derives from the high promotion energy associated with the neutral scandium atom. The lowest energy $3d^2 4s^1$ state of this atom lies 11 520 cm^{-1} above the $3d^1 4s^2$, $^2D_{3/2}$ ground state,⁵⁹ making promotion of both scandium atoms energetically quite unfavorable for the ground state of Sc_2 . In contrast, only 6557 and 2112 cm^{-1} , are required to excite titanium and vanadium atoms to their $4s^1$ configurations,⁵⁹ respectively, making $4s\sigma^2 4s\sigma^*$ configurations quite achievable in the ground states of Ti_2 , TiV , and V_2 . In ScCr , on the other hand, the ground state of Cr is $3d^5 4s^1$, which is ideally set up for bonding. However, 11 520 cm^{-1} is still required to promote the single Sc atom to the $3d^2 4s^1$ configuration, and the smaller size of the $3d$ orbitals in chromium makes them less accessible for chemical bonding than the $3d$ orbitals of scandium. Furthermore, the high spin $3d^5$, 6S core of chromium is strongly stabilized by favorable exchange interactions, and interaction with a $3d^2 4s^1$ scandium atom would lead to loss of exchange energy as $d-d$ bonds are formed. Apparently the bonding energy to be gained by promoting the scandium atom to the $3d^2 4s^1$ configuration is insufficient to make up for the energetic cost of this promotion in the ScCr molecule.

Although Sc_2^+ possesses a $4s\sigma_g^2 3d\sigma_g^1 3d\pi_u^2$, $^4\Sigma_g^-$ ground state, the promotion energy associated with this configuration is much less than that required for a $4s\sigma_g^2 4s\sigma_u^*$ configuration in neutral Sc_2 . Promotion of both Sc atoms to $3d^2 4s^1$ configurations in Sc_2 requires $2 \times 11\,520 = 23\,040$ cm^{-1} , while for $\text{Sc}+\text{Sc}^+$, the $3d^1 4s^2$, $^2D_{3/2}+3d^2$, 3F_2 separated atom asymptote lies only 4803 cm^{-1} above ground state atoms.⁵⁹ The low energy of this favorable separated atom asymptote probably makes Sc_2^+ considerably more strongly bound than Sc_2 , and implies that the ionization potential of Sc_2 is probably considerably less than that of the scandium atom.

We also note that Y_2 seems to be rather different than Sc_2 . Although numerous attempts were made, no ESR spectra could be obtained for Y_2 , Y_2^+ , or Y_2^- , despite the observation of strong matrix ESR signals due to the doublet ($S=1/2$) radical, Y_3 .⁶⁰ The energetics of the $d^1 s^2$, $d^2 s^1$, and d^3 manifolds are similar for yttrium and scandium, and the two atoms are similar in ionization poten-

tial⁵⁹ and electron affinity as well,⁶¹ making it difficult to rationalize why the corresponding yttrium and scandium molecules should have different electronic ground states. Perhaps the single most significant difference between the two atoms is that the ratio of the nd to the $(n+1)s$ orbital radii (as obtained for the d^1s^2 configuration in a relativistic Dirac-Fock self-consistent field method) is much larger for yttrium ($\langle r_{4d} \rangle_Y / \langle r_{5s} \rangle_Y = 0.596$) than for scandium ($\langle r_{3d} \rangle_{\text{Sc}} / \langle r_{4s} \rangle_{\text{Sc}} = 0.429$).⁶² This makes the d orbitals of yttrium much more accessible for chemical bonding than those of scandium, since they are not so deeply buried in the outer s orbital. The greater strength of the $4d$ orbital contributions to the bonding in Y_2 could then lead to a ground state of $5s\sigma_g^2 4d\sigma_g^2 4d\pi_u^2$, $^3\Sigma_g^-$; $5s\sigma_g^2 4d\sigma_g^2 4d\pi_u^2 4d\delta_g^1$, $^5\Delta_g$; or possibly even $5s\sigma_g^2 4d\pi_u^4$, $^1\Sigma_g^+$ (in all cases we note that the σ_g orbitals probably involve a significant amount of $so-d\sigma$ hybridization). Similar speculations would apply to the Y_2^+ and Y_2^- molecules, except in these cases the inability to observe the molecule by ESR methods is more definitive, since the molecules have an odd number of electrons, and therefore a Σ state (whether it is $^2\Sigma$, $^4\Sigma$, $^6\Sigma$, etc.) should be observable. In contrast, it is conceivable that if the ground state of Y_2 were $^5\Sigma$ or $^3\Sigma$, it might be unobservable by ESR methods if the zero-field splitting were large.

We now turn to the photodestruction behavior of Sc_2 , which could in principle provide information about the Sc_2 bond energy. As shown in Fig. 5, the neutral scandium dimer is destroyed upon photolysis by exposure to light with $\lambda < 665$ nm, which corresponds to a photon energy $h\nu > 1.86$ eV. It seems reasonable that the molecule is destroyed by a photodissociation process, so this implies $D_0^0(\text{Sc}_2) \leq 1.86$ eV, which is in accord with all previous estimates of the bond strength.^{37,39} The absorption spectrum of Sc_2 isolated in an argon matrix, shows a strong absorption at 662 nm,³⁵ and it is probably absorption into the tail of this band that causes photodissociation in the present experiments.

The characteristic ESR spectrum of Sc_2^+ can likewise be destroyed by photolysis, but in this case irradiation with wavelengths to the red of 647 nm is ineffective in destroying the molecule, while wavelengths in the range of 625–647 nm successfully convert the characteristic ESR spectrum of Sc_2^+ to that of Sc_2 . Presumably a photon energy of 1.95 ± 0.03 eV (corresponding to 625–647 nm light) is required to release an electron trapped on a matrix isolated anion, enabling it to neutralize the Sc_2^+ cation. The measurement of a threshold for this process then gives no information about the Sc_2^+ molecule itself.

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